OFFICE OF NAVAL RESEARCH

END-OF-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

Contract N00014-92-J-1183, Mod/Amend P00001

R&T Code 413d017

Fabrication and Characterization of Pt and Pt-Ir Ultramicroelectrodes

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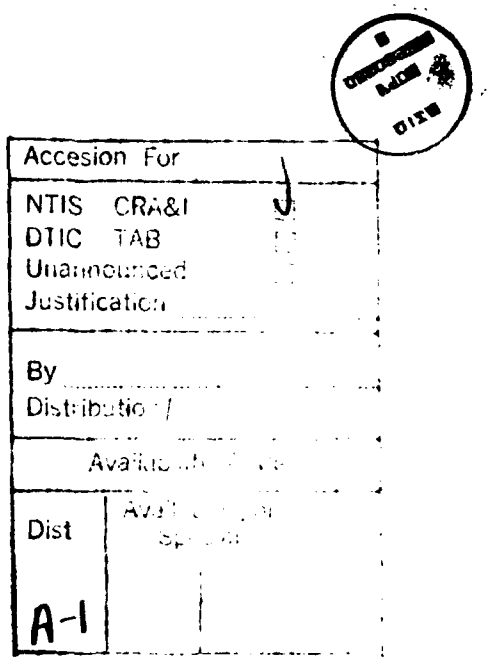
Pasadena, California 91125

May 31, 1992

CERTIFICATION OF TECHNICAL DATA CONFORMITY

The Contractor, Nathan S. Lewis hereby certifies that, to the best of his knowledge and belief, the technical data delivered herewith under Contract No. N00014-92-J-1183, Mod/Amend: P00001/R&T Code 413d017 is complete, accurate, and complies with all requirements of the contract.

Dated May 31, 1992
Name and Title of Certifying Official Nathan S. Lewis, Professor of Chemistry.



OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 413d017
Contract/Grant Number: N00014-92-J-1183, Mod/Amend P00001
Contract/Grant Title: Fabrication and Characterization of Pt and Pt-Ir Ultramicroelectrodes
Principal Investigator: Nathan S. Lewis
Mailing Address: Caltech 127-72
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Phone Number: (818) 356-6335 Fax Number: (818) 585-0147
E-mail Address: None

a. Number of papers submitted to refereed journals, but not published: 0
b. * Number of papers published in refereed journals (list attached): 0
c. Number of books or chapters submitted, but not yet published: 0
d. * Number of books or chapters published (list attached): 0
e. * Number of printed technical reports & non-refereed papers (list attached): 1
f. Number of patents filed: 0
g. * Number of patents granted (list attached): 0
h. Number of invited presentations at workshops or professional society meetings: 0
i. Number of presentations at workshops or professional society meetings: 0
j. * Honors/Awards/Prizes for contract/grant employees (list attached): 0
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.
k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:
Graduate Students: 0
Post-Doctoral Associates: 1
including the number of,
Female Graduate Students: 0
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
l. * Other funding (list agency, grant title, amount received this year, total amount, period of performance and relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published
Also submit these lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PART I

e. List of printed technical reports and non-refereed papers:

Fabrication and Characterization of Pt and Pt-Ir Ultramicroelectrodes. George J. Cali. End-of-the-Year Technical Report No. 13.

Part III.

The three viewgraphs requested for this section are enclosed: an introductory viewgraph, a viewgraph outlining the method used for the characterization of freshly etched Pt and Pt-Ir ultramicroelectrode tips, and a concluding viewgraph.

The introductory viewgraph lists the characteristics, advantages and limitations, and some potential practical applications of ultramicroelectrodes.

The second viewgraph outlines the procedure used for the characterization of freshly etched Pt and Pt-Ir ultramicroelectrode tips before sealing in glass. Application of the method to micrographs obtained by scanning electron microscopy shows that the NaOH/KCN electrochemical etch used can produce Pt and Pt-Ir ultramicroelectrode tips with hemispherical radii of respectively 0.36 ± 0.20 μm and 0.57 ± 0.24 μm (95% confidence limits). These results confirm earlier estimates and require the differentiation of ultramicroelectrodes with apparent electrochemical radii of less than 0.1 μm in two categories, nanometer-sized electrodes (nanodes) and Site Exclusion Electrochemical Detectors (SEEDS). Nanodes can be used to address fundamental questions in interfacial electrochemistry, for example the measurement of contributions due to solvent relaxation effects to reorganization energies. SEEDS may find important uses in the study of chemical and mass-transport properties in confined spaces; restricted mass transport may have important ramifications in the understanding of corrosion rates through cracks or fissures in metals resulting from metal fatigue, stress fractures, or defective welds, and also in the accurate determination of the efficiencies of batteries and flow-through catalytic systems.

Some of these issues are addressed in the concluding viewgraph.

Pt and Pt-Ir Ultramicroelectrodes

Characteristics:

- small size, 0.5-10 μm
- hemispherical or conical geometry
- mass-transport by radial diffusion

Advantages:

- low limit of detection
- high mass transport velocity
- fast transient response
- high spatial resolution

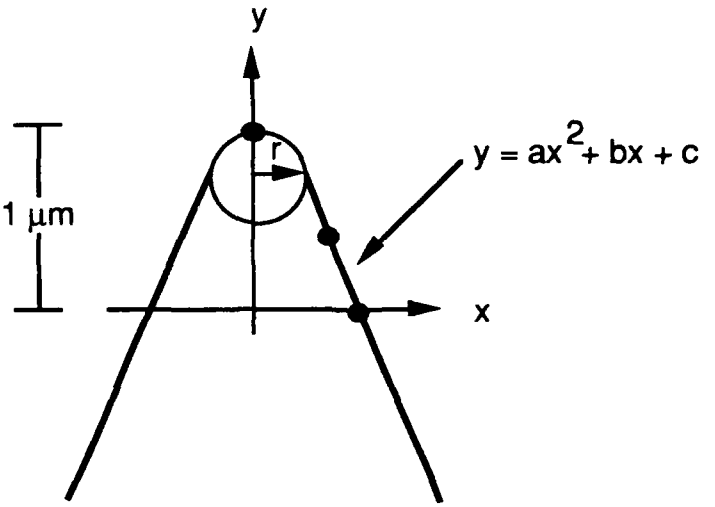
Limitations:

- response sensitive to size and geometry
- variable size distribution during manufacture
- limited life

Applications:

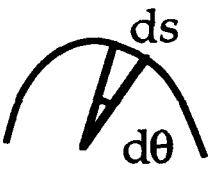
- detectors in resistive media
- sensors inside microorganisms
- micromachining tools
- microarray devices

Characterization of Etched UME Tip Geometry



Definition of curvature

$K = d\theta/ds$



$$K_{parabola} = 2a/(1 + b^2)^{3/2} \qquad (\text{at } x = 0)$$

$$K_{circle} = 1/r$$

Set $K_{parabola} = K_{circle}$ to obtain UME tip radius r

CONCLUSIONS

Pt and Pt-Ir Ultramicroelectrodes

SEM--freshly etched wires (95% confidence limits)

- Pt 0.36 ± 0.20 μm
- Pt-Ir 0.57 ± 0.24 μm
- smooth surface 40,000x magnification

Cyclic Voltammetry--after encasing in glass

- electrochemical radii 0.1-20 μm
- conical and hemispherical diffusion

Nanodes (Nanometer-sized electrodes)

- heterogeneous electron transfer rate constants
- solvent relaxation effects

SEEDS (Site Exclusion Electrochemical Detectors)

- mass transport in confined spaces
- corrosion rates: metal fatigue, welds, fractures
- efficiencies of batteries, flow-through catalysts